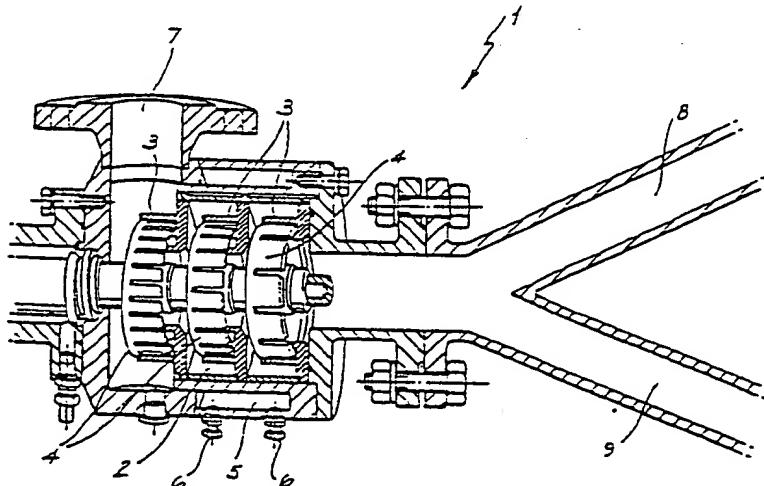




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(54) Title: PRESERVATIVE COMPOSITION



(57) Abstract

Stable emulsions and their use for preserving cellulosic materials such as timber and for applying toxicants. Stable emulsions are produced by simultaneously bringing together and emulsifying water and oil phases under conditions of ultra high shear, wherein the emulsion also contains at least one cationic, non-ionic and/or amphoteric emulsifying agent which functions without a chemically antagonistic reaction occurring. The invention also relates to an apparatus for producing emulsions which facilitates the emulsification process by providing an inlet enabling the hydrophobic and hydrophilic phases the minimum possible residence time in contact with one another prior to emulsification. The apparatus (1) has emulsifying or dispersing chamber (2) containing stators (3) and rotors (4), and an outlet (7) for emulsions. A heating or cooling jacket (5) having inlet and outlet ports (6) surrounds the chamber. Inlets (8) and (9) for the hydrophobic phase and hydrophilic phase, respectively, are provided.

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PRESERVATIVE COMPOSITION

TECHNICAL FIELD

The present invention concerns stable emulsions particularly useful for preserving timber, and for the treatment of other substrates. The invention also relates to methods of preparing these emulsions and to apparatus for manufacturing the emulsions. More particularly, the present invention concerns stable emulsions of oil and water, where the oil may be a petroleum oil, or high temperature creosote, for example.

The method of manufacturing these stable emulsions involves emulsifying the components under conditions of ultra high shear simultaneously with the bringing together of the prepared water and oil phases. This method can be conducted in a novel emulsifying apparatus of the Ultra-Turrax or Dispax-Reactor type having a specially modified inlet, so that the prepared oil and water phases are separately and simultaneously introduced into the dispersing chamber of the high speed emulsifier.

BACKGROUND ART

Compositions to protect wood and other substrates are well known in the art. One composition for preserving wood in use for over the last 300 years is creosote, as evidenced by an English Patent No. 214 which was issued to Becker and Serle in 1681. Creosote has mainly been used to preserve wood and fabric, but is also utilised in the fields of medicine, pharmacy, dyes, chemicals, carbon blacks and fuels. However, there are problems in the use of creosote; primarily with handling the substance itself, and handling articles which have been coated or treated with it, particularly due to its odour, and skin irritation caused by coming in contact with it.

In addition, other oils such as petroleum oil and vegetable oil, sometimes mixed with one or more biologically active ingredient, have been used in preserving wood and related substances.

The disadvantages in using oils such as creosote and mineral oil for preserving timber and other substances in recent times are those of heating costs in plant use, flammability, odour, pollution, and unacceptable oily, tarry or "crud" deposits coated on the surface of the treated substance. These disadvantages limit the use of oils, and creosote in particular, to the treatment of timber which is unlikely to come into contact with people or livestock.

There is therefore a need to provide a preservative composition comprising oils such as creosote which overcomes or at least ameliorates these problems.

SUBSTITUTE SHEET

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The present invention is directed to stable emulsions containing creosote or other oils to preserve lignocellulosic and other substrates in a variety of formulations and treatments and minimising the disadvantages of prior known preservative compositions leaving a black, easily removed, surface deposit, not fully drying, bleeding, staining, irritating skin, producing an unpleasant odour, having excessive flammability, and causing pollution, as well as the high energy costs involved. The potential benefits inherent in a cleaner creosote or other oil based preservative for timber and other substances are far reaching and extremely diverse.

The past use of high temperature creosote (HTC) treated products has led to complaints in Australia since the introduction of HTC in 1969. It was found that treated poles bled profusely in hot weather and developed tenacious, greasy or tarry glossy surfaces, termed "crud". The HTC caused skin sensitisation, irritation and burning on many people handling the treated timber. Similar experiences have been found in other countries with creosote treated products. Despite extensive work in various parts of the world to understand how these problems come about, until recently there have been few advances in producing a commercially acceptable improved oil or creosote based preservative composition.

Australian Patent 514897 to Koppers Australia Pty Ltd, filed on 6 September 1976 discloses oil-in-water emulsions of creosote containing pre-dispersed micronised pigments, the emulsions being produced under conditions of ultra high shear. While the compositions disclosed in this patent are very useful in many situations, problems were found during their use in connection with their stability.

Other wood preservative compositions including creosote, having improved stability over those described in Patent 514897, are disclosed in International Patent Application PCT/AU84/00103 to Koppers Australia Pty Ltd and CSIRO, filed on 13 June 1984 having International Publication No. WO85/00040. This specification particularly concerns pigment emulsified creosote (PEC) compositions which are particularly stable emulsions of creosote and water, together with micronised pigments, rheology structuring agents, wood derived resin alkali metal salts, surfactants, lignin sulfonate and a pigment modifying resin. These emulsions are also produced under conditions of ultra high shear.

DISCLOSURE OF THE INVENTION

The present invention concerns stable emulsions produced under conditions of ultra high shear and containing oils such as creosote or petroleum or mineral oil, for example, and water, together with other

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ingredients, which exhibit special qualities. The emulsions may be cationic, non-ionic, acid tolerant, anionic and/or amphoteric in nature. These qualities confer unique drying characteristics to timber, or other substrates treated with the composition. The means of treatment may be by soaking, dipping, brushing, spraying, or pressure impregnation. The pressure impregnation can be carried out under various conditions including Rüping, Lowry or Bethell schedule treatments. The emulsions of the present invention have very good stability in storage and in use, even under hostile conditions of pH, temperature, pressure, shear, flow, vacuum and contamination. The emulsions of the invention can be used on a variety of substrates in addition to wood, and result in rapid and permanent surface drying, without bleeding or the formation of undesirable surface deposits or crud. These emulsions exhibit reduced vapour pressure and odour. The odour dissipates rapidly upon drying of the treated articles and as well there is substantial fixation of the components within the treated substrate.

The composition can be used to treat such materials as wood, wood fibre, composite wood products, masonry, iron or steel and so on.

One aspect of the invention concerns a stable emulsion of water and at least one oil, produced by simultaneously bringing together and emulsifying said water and said oil under conditions of ultra high shear, wherein said emulsion also contains:

at least one cationic non-ionic and/or amphoteric emulsifying agent, which emulsifies said emulsion without a chemically antagonistic reaction occurring,

preferably at least one cation tolerant rheology structuring agent, and

preferably at least one polar chemical and/or biologically active ingredient, and preferably wherein said emulsion has a pH between 9 and 2.

The emulsion may also contain at least one hydrophobic agent and/or structuring agent introduced mixed and reacted with the oil. In addition, the composition may include one or more of pigments, fillers, extenders or bridging agents. In addition, an acid or base may need to be added to adjust the pH of the composition within a pH range of 9 to 2.

Another aspect of the invention concerns a process for the manufacture of the stable emulsion of water and at least one oil, said process comprising the steps of:

(a) preparing an aqueous phase preferably having a pH between 9 and 2 by the steps of:

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(a)(i) if present, dissolving at least one cation tolerant rheology agent in water and allowing the resulting solution to solvate for at least 24 hours with continuous gentle agitation to avoid aeration,

(a)(ii) adding and dissolving at least one cationic non-ionic and/or amphoteric emulsifying agent in the solution resulting from step (a)(i), said emulsifying agent able to emulsify the product emulsion without a chemically antagonistic reaction occurring.

(a)(iii) if present, adding and dissolving at least one polar chemical and/or biologically active ingredient in the solution resulting from step (a)(ii), and dispersing and homogenizing the solution from step (a)(iii) for at least 4 hours,

(b) preparing an oil based phase comprising at least one oil,

(c) simultaneously bringing together and emulsifying said aqueous solution and said oil based solution under conditions of ultra high shear to produce a stable emulsion.

If desired, the process may include the additional steps of:

(a)(iv) adding and dissolving at least one bridging agent in the solution resulting from step (a)(ii), and/or

(a)(v) individually or in combination adding and dispersing pigment, fillers or extenders in the solution resulting from step (a)(ii) or (a)(iv) and if necessary,

(a)(vi) adding acid or base to the solution resulting from step (a)(v) sufficient to adjust the pH within the range 9 to 2.

The process may optionally also include the steps of:

(b)(i) adding and reacting under high shear at least one hydrophobic and/or structuring agent in said oil for at least 4 hours.

(b)(ii) individually or in combination, adding and dispersing pigment, fillers, or extenders in the solution resulting from step (b)(i).

Yet another embodiment of the invention concerns an apparatus for ultra high shear emulsification of hydrophobic and hydrophilic phases, of the "Dispax-Reactor" or "Ultra-Turrax" type, said apparatus characterised by its inlet being modified so as to allow the hydrophobic and hydrophilic phases the minimum possible residence time in contact with one another prior to said emulsification; the modification comprising means for separately and substantially simultaneously introducing said phases into the emulsification chamber.

The preferred means for separately and substantially simultaneously introducing the phases into the emulsification chamber is to locate the inlet lines for the two separate phases immediately adjacent to the inlet

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to the "Dispax-Reactor" or "Ultra-Turrax" emulsification chamber. When each phase is fed at controlled rates into the chamber, they will first come in contact with each other in the chamber.

The flow rates of each phase is preferably precisely controlled according to the relative amounts in the phases required for the desired product; whether a water-in-oil or oil-in-water emulsion is required. The flow rates may be controlled by using proportional controller valves on each inlet line.

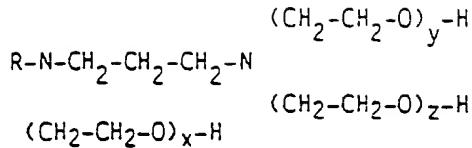
The stable emulsions of the invention are highly effective in treating and preserving wood, masonry such as reinforced concrete, steel and similar materials. Micronized pigments may or may not be included in the emulsions as a means of enhancing substantial fixing of the chemical and/or biologically active ingredients in or on the treated article. The pigments may also include fillers or extenders or additional colouring agents.

The emulsions include at least one oil. The oil may be creosote which contains a complex mixture of organic compounds and which is obtained from wood, coal, coal tars or petroleum feed stock. The oil may also be a petroleum oil, a petroleum oil fraction, or blends thereof. Vegetable oil may also be used if desired. If creosote is used, high temperature creosote (HTC) is preferred. The preferred amount of oil in the stable emulsion is from 5 to 95 weight percent. Mixtures of oils can be used, such as a mixture of creosote with a petroleum oil fraction, and/or a vegetable oil.

The stable emulsion also includes a water phase. Preferably the water used to create the emulsion does not contain very many dissolved salts, and if hard water is used, it is preferred to have the water softened prior to use. Preferably from 5 to 95% by weight of the emulsion may be water.

The stable emulsion of the invention also includes a cationic non-ionic and/or amphoteric emulsifying agent. The term "emulsifying agent" relates to those surfactants and emulsifiers which assist in dispersing a hydrophobic and hydrophilic mixture of substances without the chemically antagonistic reaction which would normally occur when such substances are mixed. Such emulsifying agents may be based upon the ethoxylated amines or fatty amines. These are most preferably ethoxylated diamines of the type:

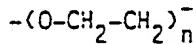
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or fatty amines of the formula $\text{R}-[\text{NH}-(\text{CH}_2)_3]_n-\text{NH}_2$ where $n = 0$ to 5. The total of substituents x , y and z may be between 3 and 100, preferably between 3 and 43 and most preferably may be 3 or 12. Substituent R is preferably tallow. The preferred ethoxylated diamines of the type described above exhibit good surfactant properties and are stable towards heat and compatible both with cations and anions. This is particularly useful where cationic toxicants and/or fire retardants are included in the emulsions. Other cationic, non-ionic and/or amphoteric emulsifiers are alkyl quaternary ammonium chlorides, imidazoline based compounds, and N -alkyl-amino-propionic acids. Preferred emulsifiers are those sold under the trade names "Dinoramox" (ethoxylated diamine) or "Stabiram". Both are manufactured by CECA, Prochimor Division, France. Preferably the emulsifier should be included in the emulsion in an amount from a trace to 10% by weight.

The emulsion of the invention may also include at least one cation tolerant rheology structuring agent. The cation tolerant rheology structuring agents are hydrophilic substances which thicken, suspend and stabilise water based systems. Such agents in solution can prevent fine solid particles from settling, or oil drops from rising and assist in bridging the density gap between the water phase and the oil phase.

A preferred rheology structuring agent is "Polyox" which is a high molecular weight, water soluble polymer of ethylene oxide, of the type:



where n is from about 2,000 to about 100,000. Polyox is stable in acid solutions, and its use is preferred in the compositions of the present invention. The structuring agent is preferably present in the composition in an amount from a trace to 2.5% by weight. Another rheology structuring agent which may be used is that sold under the trade mark "Kelzan" by the Kelco Company of the United States, which is a xanthan gum. Swelling clays such as "Premium Gel" may also be used. Examples of other rheology structuring agents are marketed under the trade names of "Carbopol", which comprise carboxy vinyl polymers, as well as "Cabosil", comprising fumed silicon dioxide.

The emulsion compositions of the present invention are non-ionic amphoteric and/or cationic in nature. The preferred formulations may

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involve the addition of an organic or inorganic acid to both react with the ethoxylated diamine to render it an emulsifier and or control pH in the final emulsion. Examples of the inorganic acid are phosphoric acid, orthophosphoric acid and hydrochloric acid which are added in an amount necessary to neutralise the ethoxylated diamine according to the number of ethylene oxide molecules condensed on the amine and to control the pH of the emulsion to between 1 and 9, preferably between 2 and 6. Examples of the organic acid are glacial acetic acid, stearic acid, linoleic acid and oleic acid.

The amount of acid utilized over and above that necessary to neutralize the ethoxylated diamine can be important when a metal oxide or hydroxide or mixture constitutes the pigment incorporated in the emulsion. The amount of acid to achieve the desired pH of the emulsion will be governed by the desired stability of the final emulsion concomitant with the isoelectric point(s) of the pigment system and oil or water droplets embodied in and in regard to behaviour of the emulsion.

The emulsion may also include at least one polar chemical and/or biologically active ingredient. Such a polar active ingredient is a substance which interacts with the structure of the substrate upon which it confers chemical and/or biological protection, or with which it reacts integral to the emulsion chemistry. Preferably such an ingredient is a highly acidic, metal cation rich, polar complex, which is also an oxidising agent. The preferred such substance is a copper-chromium- arsenic paste or liquid sold under such trade names as "Tanalith", "Celcure" and "Boliden". Other polar active ingredients are water soluble boron, fluorine compounds and so on, or these are substituted in the copper-chromium compounds above, for example. The polar active ingredient is preferably present in an amount of a trace to 25% by weight.

The ingredients may also include one or more bridging agents. A bridging agent is a compound which is soluble in both phases, and which reduces the mutual repellent nature of the individual phases comprising the emulsion. The preferred bridging agent is a glycol, most preferably hexylene glycol. If used, the bridging agent should be present in an amount from a trace to 30% by weight.

One or more predispersed micronized pigments may also be included in the composition of the invention. The pigment may be an amphoteric, nonionic or cationic pigment. Pigments includes fillers, extending and colouring agents. A preferred pigment is titanium dioxide. More than one micronized pigment can be used. These pigments may be precoated and

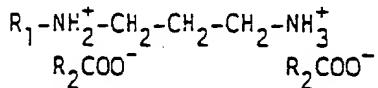
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activated with one or more cationic or amphoteric surfactants to allow the pigment to be easily dispersed in the aqueous and/or oil phase and to be electrically active. If a precoated pigment is used, it is preferably included in an amount from 0.5 to 7.5 weight percent. Alternatively, the micronized pigments may be predispersed in an amphoteric nonionic or cationic medium in a concentration of up to 75 weight percent, and this solution incorporated in the composition of the invention so that the pigment comprises from 0.5 to 30 weight percent.

In whatever way the pigment is pretreated or incorporated in the composition, if present it is preferably in an amount from 0.5 to 30 weight percent. More preferably, it is present in an amount less than 25 weight percent. Other pigments incorporated in the specification may be organic pigments or metallic pigments, such as bronze powder or aluminum paste, and various types of fillers such as talc, silicon dioxide and calcites.

When an oil is present which is not creosote, or as a frequently desirable option when creosote is present, extra substances may be present in the emulsion.

One of these substances is a hydrophobic and lipophilic agent which is reacted in the oil phase prior to emulsification. A hydrophobic agent is a compound which chemically activates the organic phase to enhance its water repellency and assist in protecting it from the hostile nature of the water phase. A preferred hydrophobic agent is a long chain aliphatic amine. These amines have the advantage of conferring corrosion resistance on the surfaces of machinery and apparatus used to produce the protective compositions, and onto the surfaces of metal substrates treated with compositions for example. These amines also are bactericides and algicides. The hydrophobic agent chosen should be cation tolerant and a preferred such amine is diamine dioleate of the type:



In this formula, R_1 is a long chain fatty acid preferably tallow or oleyl and R_2 is preferably derived from oleic acid, or similar acids.

Preferred hydrophobic agents are those sold under the trade names "Inipol 002" or "Inipol S02". Both compounds are manufactured by CECA, Prochimor Division, France. The hydrophobic agent is preferably present in the composition in amount from a trace to 10% by weight, and preferably from 0.2 to 1.0% by weight. One or more predispersed micronised pigments may be dispersed into the oil phase. These pigments are preferably included in an amount of from 0.5 to 7.5% by weight.

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The compositions of the invention are capable of continuous use under normal and adverse conditions of temperature and pressure and are able to withstand significant contamination by inert materials, opposing ions and chemicals and acid extractives from the timber substrates.

Desirable optional components in the composition of the invention are pre-treated and/or pre-coated micronized pigments or extenders or inert fillers capable of reaction within the emulsion and on or within the structure of the substrate to produce special effects.

Either the oil phase, and/or the water phase, can be modified chemically or fortified by the addition of water and/or oil soluble toxicants, and/or phase-dispersed insoluble toxicants to provide insecticidal and termicidal efficacy concomitant with a clean, non-oiluting and aesthetically pleasing treated substrate. Other ingredients can also be added to the composition to confer the broad spectrum of activities required in the building industry field. Paraffin waxes of various melting point specification from 47°C through 127°C, beeswax (crude or refined), water soluble waxes of various grading and molecular weight may be added to the emulsions of the invention in proportion of up to 10% by weight of final emulsion. These waxes can be added individually or in combination dictated by finished emulsion and its desirable inherent qualities. The waxes can be added in the form of crude petroleum wax. The waxes are added to provide enhanced water-proofing.

Fillers which may be useful in the emulsions of the invention are e.g. Reynolds (USA) sodium aluminate powder, talc, diatomaceous earth, calcite, barytes, and silicates.

Dyes useful in the emulsions of the invention are oil soluble dyes which are used alone or in conjunction with pigments to heighten colour upon ageing, or upon initial application and to protect the finished product by deflecting some specific wavelengths light, inhibit u.v. effects and prevent tar-like exudate formation or inhibit oxidation. Dyes can be used in the compositions of the invention in a sacrificial mode to screen out u.v. and/or i.r. radiation in initial stages of exposure of painted or treated surfaces so that fading occurs to heighten pigment colouration and precludes any tar formation or darkening. Examples of suitable dyes are INTERACETYL RED, INTERACETYL GREY, KCA oil yellow 2G, KCA oil orange E, KCA oil red A, CHROMOFINE orange 2R550, CHROMOFINE red B750, SEIKAFAST yellow M35, CHROMOFINE GREEN 2G550D and CHROMOFINE BLUE 5275.

The metallic pigments have found excellent use in imparting a "metallic" and lustrous finish alone or in conjunction with other

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colourants. This function of the compositions of the invention not only relies upon penetration of, and preservative value of, the creosote but provides added mechanical protection to surfaces for areas of exposure to severe conditions of environmental hazards such as dust, water, salt, fall-out, salt spray, chemical attack, etc. Suitable metallic pigments are e.g. bronze powders and aluminium pastes. The pastes may be used in amounts of up to 10% alone or in combination with pigments and/or dyes.

Vegetable oils used additionally in the emulsions of the invention are oils derived from natural products and used as emulsion stabilisers, drying aids, extenders and solution aids for specific high resin additions. These oils are used to ensure compatibility of some non-aromatic ingredients where long storage life is expected. They have been used to change vapour pressure characteristics of finished emulsion which is subsequently used in livestock areas or high density housing and population areas. They are used to assist in forming metal soaps. Some examples of these vegetable oils are tall oil, tallow fatty acids, fatty acid pitch, crude linseed oil, boiled linseed oil, polymerised linseed oil, soya bean oil, rapeseed oil, wood oils, stand oils, castor oil, stearic fatty acids and coconut fatty acids.

These oils may additionally be added in amounts up to 10% of the finished emulsion and for specific purposes up to 25% of the finished emulsion.

Mineral oils may be useful as additives in the emulsions of the invention to reduce the aromatic content of the emulsion or to enable specific formulation and difficult resin additions to be made. Examples of these mineral oils are mineral turpentine, paraffin oil, low aromatic oils, liquid paraffins, modified process oils, diesel fractions (kerosene cuts), process oils. These oils may additionally be added in amounts up to 10% of finished emulsion and to higher percentages for specific extender or solution aid uses.

The emulsions of the invention may be applied to porous substrates, by impregnation at ambient or elevated pressures and at ambient or elevated temperatures. The emulsions may also be applied to surfaces by spraying, brushing or rolling. The viscosity of the emulsion may be adjusted so that the compositions have the consistency of a fluid-paste, wax or gel. When the emulsions are in those forms they may also be applied to surfaces by rubbing, trowelling, pumping and so on.

The invention provides an ultra stable emulsion which can be modified by addition of inert fillers, specialised chemicals and non-flammable

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organic liquids and complex solutions, colloids and/or other emulsions to impart fire retardancy to the treated timber. Especially significant is the range of fire retardant organic liquids which can be dissolved in and/or emulsified with the creosote to produce a fire retardant preservative with none of the vapour problems associated with some of the organic liquids alone. Some fire retardant chemicals which can be emulsified in the invention do exhibit inherent preservative efficacy and would complement the compositions of the invention.

One method of preparing the composition involves dissolving the cation tolerant rheology agent in water with continuous gentle agitation and allowing the resulting solution to solvate for at least 24 hours. At the end of this period, the cationic non-ionic and/or amphoteric emulsifier is added to the solution, with continuous agitation and letting it react for a minimum of one hour.

The water phase is agitated continuously during this period. When a bridging agent is used, it is added to the water phase and ideally allowed to mix for about one hour. If a pigment is required, it is added to the solution so as to avoid foaming. Ideally the mixture is allowed to react for 2 hours prior to the addition of the polar chemical and/or biologically active ingredient. The completed aqueous phase solution should preferably be allowed to age for at least four hours, before being mixed with the oil based phase.

The oil based phase is prepared separately comprising at least one oil. The oil may be a petroleum oil, or creosote, or a mixture of these, for example. The hydrophobic agent, if included, may be dissolved and reacted in the oil, preferably in hot oil at a temperature of 40 to 50°C. If a pigment is desired, it is dispersed in the oil phase prior to ageing. The resulting oil based phase should ideally be allowed to age for at least four hours, before emulsification.

The other ingredients may be added to the oil or aqueous phases at this stage, depending on whether they are hydrophobic or hydrophilic. The emulsion is prepared by simultaneously bringing together and emulsifying the aqueous and oil phases under conditions of ultra high shear. The ultra high shear conditions may be produced using a Dispax-reactor or an Ultra-turrax reactor, having an inlet which has been modified so that the two phases are mixed together for an absolute minimum time prior to actual emulsification. This is preferably done by only bringing together the two different phases at the actual time when emulsification occurs, by means of two separate pipes bringing each phase

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straight into the suction of the reactor inlet.

The ultra high shear may be carried out by any means known in the art for such a purpose.

However, the ultra high shear emulsification is preferably carried out using a novel apparatus in accordance with one embodiment of the present invention.

The apparatus is generally of the Dispax-Reactor or Ultra-turrax type with modifications to allow the separate and simultaneous introduction of the prepared hydrophilic and hydrophobic phases into the dispersing chamber of the apparatus. The Dispax and Ultra-turrax apparatus are based on the effect of mechanical high-frequency on stator/rotor systems at high peripheral speeds. Their dispersing chambers, where the stable emulsions are produced, generally contain slotted cylinders, the slots arranged parallel to the axis of rotation. The cylinders are closely spaced to the walls of the chambers, and rotate at very high speeds.

The means for introducing the two different phases into the central space of the cylinders may be a jet arrangement, or preferably two separate input conduits meeting at the entrance to the dispersing chamber, or other means.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a sectional view of a modified Dispax-Reactor apparatus for ultra high shear emulsification to produce the stable emulsion of the invention.

Figure 2 shows a more complete view of the apparatus of Figure 1 for ultra high shear emulsification to produce the stable emulsion of the invention, and showing how flow rates of the two phases are adjusted and controlled.

BEST MODE FOR CARRYING OUT THE INVENTION

Various embodiments of the present invention are now described with reference to actual examples which should not be construed as limiting on the present invention.

Examples 1 to 6

The following examples were blended in an Ultra Turrax reactor in accordance with the invention, using a T45 G6 Generator at 1050 rad.
 sec^{-1} at room temperature (about 20°C) to produce cationic emulsions as listed in Table 1

- A Water
- B Polyox WSR205 [Rheology structuring agent]
- C Hexylene Glycol [Bridging agent]

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- D Dinoramox S12 [Emulsifying agent]
- E Non-ionic pigment (white) [Pigment]
- F High Temperature creosote (AS1143) [Oil]
- G Inipol 002 [Hydrophobic agent]

TABLE 1

| Example Number | A | B | Component (parts by weight) | C | D | E | F | G | pH * |
|----------------|------|------|-----------------------------|-----|-----|------|-----|-----|------|
| 1 | 27.5 | 0.25 | 2.5 | 1.0 | 5.0 | 70.0 | 1.0 | 5.8 | |
| 2 | 27.5 | 0.25 | 2.5 | 1.0 | 5.0 | 70.0 | 1.0 | 3.9 | |
| 3 | 27.5 | 0.25 | 2.5 | 1.0 | 5.0 | 70.0 | 1.0 | 2.0 | |
| 4 | 47.5 | 0.5 | 2.5 | 1.0 | 5.0 | 50.0 | 1.0 | 6.0 | |
| 5 | 47.5 | 0.5 | 2.5 | 1.0 | 5.0 | 50.0 | 1.0 | 3.8 | |
| 6 | 47.5 | 0.5 | 2.5 | 1.0 | 5.0 | 50.0 | 1.0 | 1.9 | |

* Using phosphoric acid as a polar chemically active ingredient and to adjust the pH.

The formulations produced in Examples 1-6 were subjected to seven cycles of freezing at -18°C for 16 hours followed by thawing for 3 hours. The emulsions remained stable visually. Prior to freeze/thaw a quantity of emulsion was removed from Examples 1-6. Those samples were heated up to 100°C for seven days then cooled to ambient temperature. The emulsions remained stable visually.

Examples 7 to 30

The following examples were blended in an Ultra Turrax using a T45G6 Generator at 1050 rad. sec⁻¹ at room temperature (about 20°C) to produce "white" cationic emulsions as listed in Table 2.

- A Water
- B Polyoxy WSR205 [Rheology structuring agent]
- C Stabiram MS3 [Emulsifying agent]
- D Non-ionic pigment (white) [Pigment]
- E High Temperature creosote (AS1143) [Oil]
- F Inipol 002 [Hydrophobic agent]
- G Calcium Chloride

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TABLE 2

| Example Number | A | B | C | D | E | F | G | pH * |
|----------------|------|------|-----|-----|------|-----|-----|------|
| 7 | 50.0 | 0.5 | 1.0 | 5.0 | 50.0 | 0.5 | 0.4 | 6.0 |
| 8 | 50.0 | 0.5 | 1.0 | 5.0 | 50.0 | 0.5 | - | 6.0 |
| 9 | 50.0 | 0.5 | 1.0 | 5.0 | 50.0 | 0.5 | 0.4 | 4.0 |
| 10 | 50.0 | 0.5 | 1.0 | 5.0 | 50.0 | 0.5 | - | 4.0 |
| 11 | 50.0 | 0.5 | 1.0 | 5.0 | 50.0 | 0.5 | 0.4 | 2.0 |
| 12 | 50.0 | 0.5 | 1.0 | 5.0 | 50.0 | 0.5 | - | 2.0 |
| 13 | 50.0 | 0.5 | 1.0 | 5.0 | 50.0 | - | 0.4 | 6.0 |
| 14 | 50.0 | 0.5 | 1.0 | 5.0 | 50.0 | - | - | 6.0 |
| 15 | 50.0 | 0.5 | 1.0 | 5.0 | 50.0 | - | 0.4 | 4.0 |
| 16 | 50.0 | 0.5 | 1.0 | 5.0 | 50.0 | - | - | 4.0 |
| 17 | 50.0 | 0.5 | 1.0 | 5.0 | 50.0 | - | 0.4 | 2.0 |
| 18 | 50.0 | 0.5 | 1.0 | 5.0 | 50.0 | - | - | 2.0 |
| 19 | 30.0 | 0.25 | 1.6 | 5.0 | 70.0 | 0.5 | 0.4 | 5.5 |
| 20 | 30.0 | 0.25 | 1.6 | 5.0 | 70.0 | 0.5 | - | 5.5 |
| 21 | 30.0 | 0.25 | 1.6 | 5.0 | 70.0 | 0.5 | 0.4 | 4.0 |
| 22 | 30.0 | 0.25 | 1.6 | 5.0 | 70.0 | 0.5 | - | 4.0 |
| 23 | 30.0 | 0.25 | 1.6 | 5.0 | 70.0 | 0.5 | 0.4 | 2.4 |
| 24 | 30.0 | 0.25 | 1.6 | 5.0 | 70.0 | 0.5 | - | 2.4 |
| 25 | 30.0 | 0.25 | 1.5 | 5.0 | 70.0 | - | 0.4 | 6.0 |
| 26 | 30.0 | 0.25 | 1.5 | 5.0 | 70.0 | - | - | 6.0 |
| 27 | 30.0 | 0.25 | 1.5 | 5.0 | 70.0 | - | 0.4 | 4.0 |
| 28 | 30.0 | 0.25 | 1.5 | 5.0 | 70.0 | - | - | 4.0 |
| 29 | 30.0 | 0.25 | 1.5 | 5.0 | 70.0 | - | 0.4 | 2.5 |
| 30 | 30.0 | 0.25 | 1.5 | 5.0 | 70.0 | - | - | 2.5 |

* Using phosphoric acid as a polar chemically active ingredient and to adjust pH.

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Examples 31 to 43

The following examples were blended in an Ultra Turrax using a T45G6 Generator at 1050 rad. sec⁻¹ at room temperature (about 20°C) to produce "white" cationic emulsions as listed in Table 3:

- A Water
- B Polyox WSR205 [Rheology structuring agent]
- C Hexylene Glycol [Bridging agent]
- D Dincramox S12 [Emulsifying agent]
- E Copper-Chromium-Arsenic paste (Taralith CP)
[Polar chemically and biologically active ingredient]
- F High Temperature Creosote [Oil]
- G Inisol 002 [Hydrophobic agent]
- H Cationic Pigment (white) [Pigment]
- I Non-ionic pigment (white) [Pigment]
- J Cabosil [Rheology structuring agent]

TABLE 3

| Example Number | Component (parts by weight) | | | | | | | | | |
|-------------------|-----------------------------|-----|-----|-----|------|------|-----|-----|-----|-----|
| | A | B | C | D | E | F | G | H | I | J |
| 31 | 78.0 | 1.0 | 2.0 | 1.0 | 8.1 | 21.0 | 1.0 | 2.0 | -- | 1.0 |
| 32 | 78.0 | 1.0 | 2.0 | 1.0 | 8.1 | 21.0 | 1.0 | 2.0 | -- | 0.5 |
| 33 | 78.0 | 1.0 | 2.0 | 1.0 | 8.1 | 21.0 | 1.0 | 2.0 | -- | -- |
| 34 | 78.0 | 1.0 | 2.0 | 1.0 | 13.0 | 21.0 | 1.0 | 2.0 | -- | 1.0 |
| 35 | 78.0 | 1.0 | 2.0 | 1.0 | 13.0 | 21.0 | 1.0 | 2.0 | -- | 0.5 |
| 36 | 78.0 | 1.0 | 2.0 | 1.0 | 13.0 | 21.0 | 1.0 | 2.0 | -- | -- |
| 37 | 78.0 | 1.0 | 2.0 | 1.0 | 8.1 | 20.0 | 1.0 | -- | 2.0 | 1.3 |
| 38 | 78.0 | 1.0 | 2.0 | 1.0 | 8.1 | 20.0 | 1.0 | -- | 2.0 | -- |
| 39 | 68.2 | 0.9 | 1.8 | 0.9 | 7.1 | 30.0 | 1.5 | -- | 1.8 | 1.3 |
| 40 | 68.2 | 0.9 | 1.8 | 0.9 | 7.1 | 30.0 | 1.5 | -- | 1.8 | -- |
| 41 | 58.5 | 0.8 | 1.5 | 0.8 | 6.1 | 40.0 | 2.0 | -- | 1.5 | 1.3 |
| 42 | 58.5 | 0.8 | 1.5 | 0.8 | 6.1 | 40.0 | 2.0 | -- | 1.5 | -- |
| 43 | 48.8 | 0.6 | 1.2 | 0.6 | 5.1 | 50.0 | 2.5 | -- | 1.3 | -- |

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Example 44

A 500kg batch of emulsion with the following components (parts by weight) was manufactured in an emulsifying pilot plant using a modified Dispax Reactor in accordance with the invention.

| Component | Parts | Amount (kg) |
|--|-------|----------------|
| A Water | 27.5 | 137.5 |
| B Polyox WSR205 [Rheology structuring agent] | 0.25 | 1.25 |
| C Heylene Glycol [Bridging agent] | 2.5 | 12.5 |
| D Dinoramox S12 [Emulsifying agent] | 1.0 | 5.0 |
| E Nonionic Pigment (White) [Pigment] | 5.0 | 25.0 |
| F High Temperature Creosote [Oil] | 70.0 | 350.0 |
| G Inipol 002 [Hydrophobic agent] | 1.0 | 5.0 |
| H Orthophosphoric acid | 1.0 | 5.0 |
| [Polar chemically active ingredient] | | |

This emulsion at an initial pH of 3.2 was used to treat hardwood pole stubs and sawn timber. Twenty treatment charges were carried out and the emulsion was heated to temperatures of up to 73°C and hydraulic pressures of up to 1400KPa were used. The pH, surface tension, specific gravity, moisture content and pigment content of the emulsion used in each charge was analysed. After 20 charges, despite slight increases in the pH and pigment values, the emulsion was still stable based on detailed analyses, macroscopic and microscopic observations.

The surface of all the treated samples dried within a few weeks in spite of the wintry conditions.

Example 45

A 300kg batch of emulsion of the following compositions using the pilot emulsion plant.

| Component | Parts | Amount (kg) |
|---|-------|----------------|
| A Water | 63.4 | 190.0 |
| B Polyox WSR205 [Rheology structuring agent] | 0.8 | 2.5 |
| C Hexylene Glycol [Bridging agent] | 1.6 | 5.0 |
| D Dinoramox S12 [Emulsifying agent] | 0.8 | 2.5 |
| E Non-ionic Pigment (White) [Pigment] | 5.0 | 15.0 |

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| | | | |
|---|--|------|-------|
| F | Copper-Chromium-Arsenic Paste [Polar chemically and biologically active ingredient] | 5.6 | 20.0 |
| G | High Temperature Creosote [Oil] | 35.0 | 105.0 |
| H | Inipol 002 [Hydrophobic agent] | 1.8 | 5.3 |
| I | Orthophosphoric acid [Polar chemically active ingredient] | 0.05 | 0.15 |

The final pH of the completed emulsion was 4.2. Five treatment charges of hardwood pole stubs were treated with this completed emulsion. At the end of this, the emulsion was still stable, according to analytical and microscopical results.

Example 46

The following were blended in an Ultra-Turrax reactor in accordance with the present invention using T45 G6 generator at 1050 rad.sec at ambient temperature (20°C).

| | Parts by Weight |
|---|--|
| A | Distilled Water |
| B | 50.0 |
| B | Polyox WSR205 [Rheology structuring agent] |
| C | 0.5 |
| C | Dinoramox S12 [Emulsifying agent] |
| D | 1.0 |
| D | Orthophosphoric acid |
| D | [Polar chemically active ingredient] |
| E | 0.5 |
| E | High Temperature Creosote [Oil] |
| F | 50.0 |
| F | Non Ionic Pigment (white)[Pigment] |
| F | 3.0 |

Example 47

The following were blended in a Ultra Turrax (as in Example 46)

| | Parts by Weight |
|---|--|
| A | Distilled Water |
| B | 45.0 |
| B | Polyox WSR205 [Rheology structuring agent] |
| C | 0.25 |
| C | Dinoramox S12 [Emulsifying Agent] |
| D | 1.0 |
| D | Orthophosphoric acid |
| D | [Polar chemically active ingredient] |
| E | 0.5 |
| E | Hexylene Glycol [Bridging Agent] |
| F | 5.0 |
| F | High Temperature Creosote [Oil] |
| G | 50.0 |
| G | Inipol 002 [Hydrophobic agent] |
| G | 0.5 |

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Example 48

The following were blended in an Ultra Turrax (as in Example (46)

| | | Parts by Weight |
|---|---|-----------------|
| A | Distilled Water | 63.5 |
| B | Polyox WSR205 [Rheology structuring agent] | 0.5 |
| C | Dinoramox S12 [Emulsifying agent] | 0.8 |
| D | Hexylene Glycol [Bridging agent] | 1.5 |
| E | Non-ionic Pigment (white) [Pigment] | 5.0 |
| F | Copper-chromium-arsenic paste [Polar chemically & biologically active ingredient] | 6.5 |
| G | Industrial Fuel Oil [Heavy residue from petroleum crude refinery] | 35.0 |

Example 49

The following were blended in an Ultra Turrax (as in Example (46)

| | Component | Parts by Weight | Amount (kg) |
|---|--|--------------------|----------------|
| A | Water | 6.5 | 325.0 |
| B | Dinoramox S12 [Emulsifying Agent] | 1.0 | 5.0 |
| C | Tanalith [Polar chemically active ingredient] | 10.7 | 5.1 |
| D | Oil (Protea 15 Oil) | 35.0 | 175.0 |
| E | Dinoramox S 43 [Emulsifying Agent] | 0.5 | 2.5 |

Other aspects of the present invention are described with reference to the drawings.

With reference to Figure 1, which shows a partial sectional view of a modified Dispax-Reactor in accordance with the present invention, a reactor 1 is shown having an emulsifying or dispersing chamber 2. The dispersing chamber 2 contains stators 3 and rotors 4. There is a heating or cooling jacket 5 having inlet and outlet ports 6 surrounding the chamber. There is an outlet 7 for the stable emulsions produced by the apparatus 1, in accordance with the invention. The apparatus 1 has an inlet 8 for the hydrophobic phase and an inlet 9 for the hydrophilic phase, the phases mixing and forming the stable emulsion in the dispersing chamber 2. The residence time of the hydrophobic and hydrophilic phases, once mixed, is kept to a minimum prior to entering the dispersing chamber. In the chamber 2 the two phases are mechanically sheared by the rotor 4/stator 3 arrangement inside the chamber 2. The rotor 4 rotates up to 8,000 rpm and

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the circumferential speed of the rotor/stator system is up to 23 m/sec. The two phases entering the chamber 2 via inlet conduit 8 and conduit 9 are pumped so that the mixture is forced to pass through the three rotor/stator generators in series, (from coarse to fine), to produce the stable emulsion of the invention.

Figure 2 shows a more complete version of the Dispax-Reactor of Figure 1. The features of the modified Dispax-Reactor in Figure 2 are numbered the same as in Figure 1.

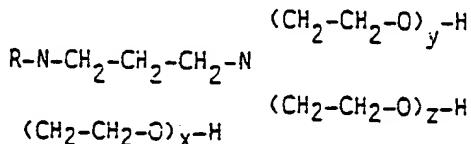
However, the apparatus also shows the electric motor 10 which powers the stator/rotor assembly. In addition, in order to manufacture an emulsion of the desired composition, namely a water-in-oil or oil-in-water emulsion, there needs to be precise control of the hydrophobic and hydrophilic phase flow rates. Figure 2 shows how the flow rates may be adjusted using control valves 11 connected to a proportional controller 12, which is used to govern the actual flow rate. Non-return valves 13 are preferably installed in the input conduits 8 and 9 to prevent backflow and mixing of one phase with the other.

The two phases are pumped simultaneously through the generator chamber at high speeds so that each of the oil and water phases is mixed together for the minimum amount of time prior to emulsification. In the normal, unmodified Dispax-Reactor, the two phases are not kept separate prior to emulsification, but are allowed to intermingle for some relatively long period of time. The normal Dispax-Reactor does not produce as stable an emulsion as the apparatus as herein described.

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CLAIMS

1. A stable emulsion of water and at least one oil, produced by simultaneously bringing together and emulsifying said water and said oil under conditions of ultra high shear, wherein said emulsion also contains at least one cationic, non-ionic and/or amphoteric emulsifying agent, which emulsifies said emulsion without a chemically antagonistic reaction occurring.
2. An emulsion according to Claim 1 having a pH of between 9 and 2.
3. An emulsion according to Claim 1 wherein at least one oil is creosote.
4. An emulsion according to Claim 3 wherein the creosote is a high temperature creosote.
5. An emulsion according to Claim 1 wherein at least one oil is vegetable oil, a petroleum oil, or a petroleum oil fraction.
6. An emulsion according to Claim 1 wherein the cationic, non-ionic and/or amphoteric emulsifiers are chosen from one or more alkyl quaternary ammonium chlorides, imidazoline based compounds, N-alkyl-amino-propionic acids and ethoxylated amines.
7. An emulsion according to Claim 6 wherein the ethoxylated amine comprises diamines of the type:



wherein the total of the substituents x, y and z are between 3 and 100 and wherein R is an alkyl derivative of fatty acid with chain length, C₈-C₂₀ and/or fatty amines of the type R-[NH-(CH₂)_n-NH₂] wherein n = 0 to 5 and R is an alkyl derivative of a fatty acid.

8. An emulsion according to Claim 7 wherein the total of the substituents x, y and z is between 3 and 43.
9. An emulsion according to Claim 8 wherein the total of the substituents x, y and z is between 3 and 12.
10. An emulsion according to Claim 1 further containing one or more additives selected from at least one of any of the following additives: cation tolerant rheology structuring agents, waxes, dyes, pigments, micronized pigments, fillers, extenders, bridging agents, polar chemical and/or biologically active ingredients, and hydrophobic and/or structuring agents, wherein said hydrophobic and/or structuring agents are introduced,

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mixed and reacted within either the oil or aqueous phase, corrosion inhibiting chemicals, and flame retarding chemicals.

11. An emulsion according to Claim 10 wherein the rheology structuring agent is a water soluble polymer of ethylene oxide, xanthan gums, swelling clays, carboxy vinyl polymers or fumed silicon dioxide.

12. An emulsion according to Claim 10 wherein the pigment is titanium dioxide and/or iron oxides.

13. An emulsion according to Claim 10 wherein the pigments are precoated and activated with one or more cationic or amphoteric surfactants.

14. An emulsion according to Claim 10 wherein the micronized pigments are predispersed in an amphoteric, non-ionic or cationic medium in a concentration of up to 75 weight percent of the pre dispersion medium.

15. An emulsion according to Claim 10 wherein the bridging agent is a glycol.

16. An emulsion according to Claim 10 wherein the polar chemical and/or biologically active ingredient is a highly acidic, metal cation rich, polar complex which is also an oxidizing agent.

17. An emulsion according to Claim 10 wherein the hydrophobic and/or structuring agent is a diamine dioleate.

18. A stable emulsion of 5-95% water and 5-95% of at least one oil, produced by simultaneously bringing together and emulsifying said water and said oil under conditions of ultra high shear, wherein said emulsion also contains up to 10% of at least one cationic, non-ionic and/or amphoteric emulsifying agent, which emulsifies said emulsion without a chemically antagonistic reaction occurring, said emulsion further comprising up to 2.5% of a rheology structuring agent, up to 25% of a polar and/or biologically active ingredient, up to 30% of a bridging agent and up to 50% of a pigment, wherein all percentages are percent by weight of the total weight of the emulsion.

19. A process for the manufacture of a stable emulsion of water and at least one oil, said process comprising the steps of:

(a) preparing the aqueous phase by adding and dissolving at least one cationic, non-ionic and/or amphoteric emulsifying agent in water, said emulsifying agent able to emulsify the product emulsion without a chemically antagonistic reaction occurring;

(b) preparing an oil based phase comprising at least one oil in which may dissolved one or more co-surfactants; and

(c) simultaneously bringing together and emulsifying said

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aqueous phase and said oil based phase under conditions of ultra high shear to produce a stable emulsion.

20. A process according to Claim 19 wherein at least one cation tolerant rheology structuring agent is dissolved in the water to be used in Step (a) and the resulting solution allowed to solvate for at least 24 hours with continuous gentle agitation to avoid aeration before step (a).

21. A process according to Claim 19 wherein after step (a), at least one polar chemical and/or biologically active ingredient is added to and dissolved in the aqueous phase and the resulting composition is homogenised and dispersed for at least 4 hours.

22. A process according to Claim 19 wherein at least one bridging agent is added to the solution resulting from the addition of the emulsifying agent.

23. A process according to Claim 19 wherein pigment, fillers or extenders are added and dispersed either individually or in combination in the solution formed by the addition of the emulsifying agent.

24. A process according to Claim 19 wherein acid or base is added at any stage during the process sufficient to adjust the pH within the range 9-2.

25. A process according to Claim 19 wherein at least one hydrophobic and/or rheology structuring agent is added to the oil based phase and reacted under high shear for at least 4 hours.

26. A process according to Claim 25 wherein pigment, fillers or extenders are added to and dispersed in the oil based phase either individually or in combination after the introduction of an hydrophobic and/or rheology structuring agent.

27. An apparatus for emulsification of hydrophobic and hydrophilic phases capable of producing an emulsion under conditions of ultra-high shear, characterized in that said apparatus is modified by means for separately and substantially simultaneously introducing said phases into an emulsification chamber, said means characterised by an inlet enabling the hydrophobic and hydrophilic phases the minimum possible residence time in contact with one another prior to said emulsification.

28. An apparatus according to Claim 27 wherein the means for separately and substantially simultaneously introducing the phases into the emulsification chamber comprises location of the inlet lines for the two separate phases feeding directly into the emulsification chamber.

29. An apparatus according to Claim 28 wherein the inlet lines contain means for controlling the flow rates.

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30. An apparatus according to Claim 29 wherein the means for controlling the flow rates comprise proportional controller valves on each inlet line.

31. A method for preserving cellulosic substances against deterioration comprising applying the emulsion according to Claim 1 to said cellulosic substances.

32. A method according to Claim 31 wherein the application is by vacuum pressure impregnation, spraying or brushing.

33. A method of applying toxicants to a cellulosic substance wherein the emulsion defined by Claim 1 is modified by the addition of water and/or oil soluble toxicants, and/or phase-dispersed insoluble toxicants.

2 SHEETS, SHEET 1

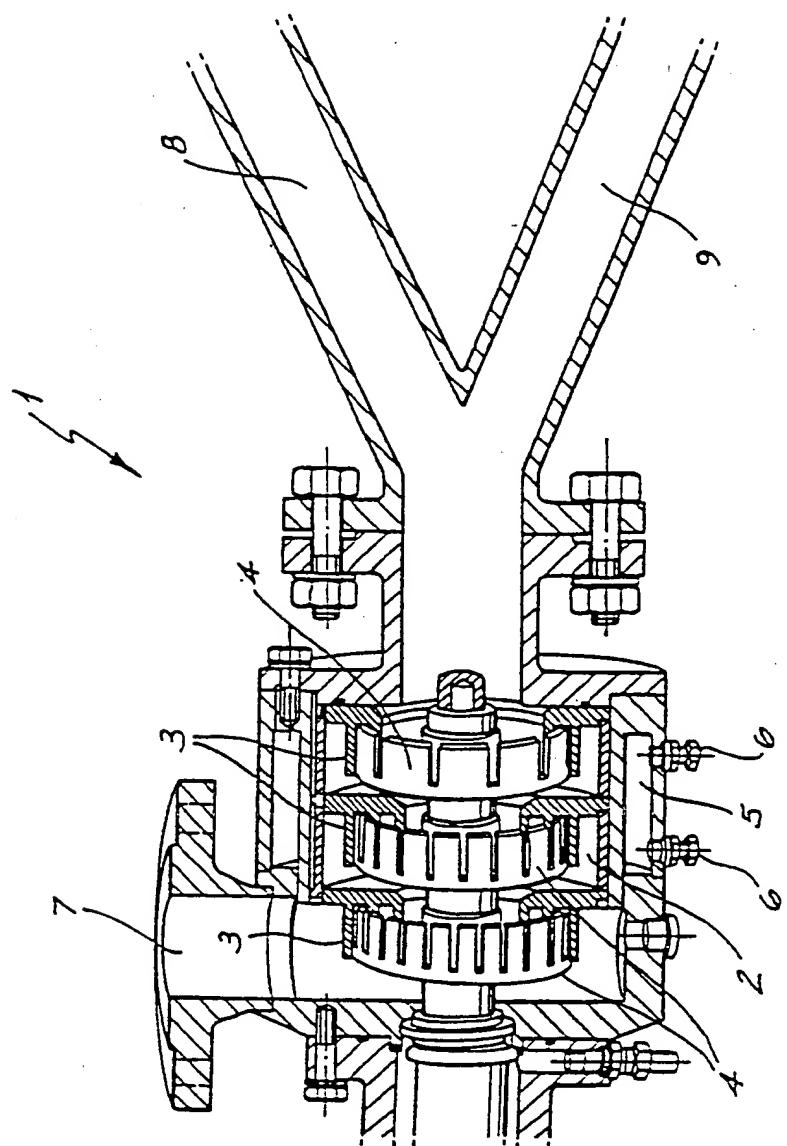


FIG. 1

SUBSTITUTE SHEET

2 SHEETS, SHEET 2

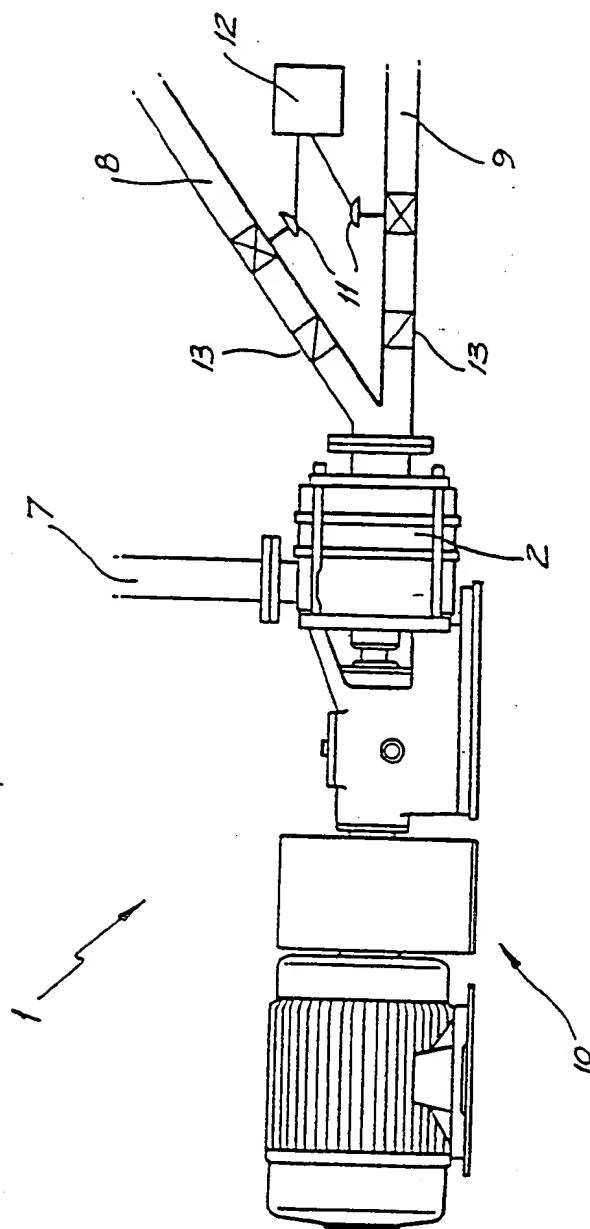


FIG. 2

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US86/02737

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ¹⁶

According to International Patent Classification (IPC) or to both National Classification and IPC
 IPC: 4 A01N 59/22; B01F 15/02; B05D 1/18; C08L 95/00; C09D 3/24, 5/14.
 U.S. Cl. 106/15.05, 244, 284, 308N; 252/309, 312, 314; 366/134, 177; 424/137; 427/441.

II. FIELDS SEARCHED

Minimum Documentation Searched ¹⁴

| Classification System | Classification Symbols |
|-----------------------|---|
| U.S. | 106/15.5, 244, 284, 308N; 252/309, 312, 314 366/134, 177; 424/137; 427/441 |

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ¹⁵

III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴

| Category ¹⁶ | Citation of Document, ¹⁸ with indication, where appropriate, of the relevant passages ¹⁷ | Relevant to Claim No. ¹⁸ |
|------------------------|--|-------------------------------------|
| Y | US, A, 1,638,440 Published 09 August 1927 HoWald See page 1, line 59-page 2, line 75. | 1-33 |
| Y | AU, B, 514, 897 Published 31 August 1977 Koppers Australia PTY. LTD. See examples 1-4 | 1-33 |
| Y | US, A, 3,748,275 Published 24 July 1973, Bernheim et al. See examples 1-7. | 1-33 |
| Y | US, A, 3,650,792 Published 21 March 1972, Dietz See column 1, lines 44-55 and col. 8, lines 15-47. | 10,12-14 23,26 |
| Y | US, A, 2,158,374 Published 16 May 1939; Merrill See page, 2D col., lines 34-56. | 10,15,22 |
| Y | N, Mc Cutcheon's Detergents and Emulsifiers 1973 No. American Edition, Issued 1973, page 3 | 10,17,25 |
| Y | US, A, 3,832,463 Published 27 August 1974 Nicholson, See abstract and col. 1, lines 21-33. | 10,16,21 |
| X | US, A, 3,635,834 Published 18 January 1972 | 27-29 |
| Y | Cilento et al., See drawing and col. 1, line 19-col.2, line 56. | 19-26,30 |

* Special categories of cited documents: ¹⁶

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"d" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search ¹⁹

03 March 1987

Date of Mailing of this International Search Report ²⁰

18 MAR 1987

International Searching Authority ¹

ISA/US

Signature of Authorized Officer ²⁰

Richard D. Lovering
Richard D. Lovering ✓